

**STANDARD OPERATING PROCEDURE (S.O.P.) FOR THE ACID EXTRACTION AND ANALYSIS OF
METALS FROM THE TOTAL SUSPENDED PARTICULATES (TSP)
COLLECTED ON EXPOSED, GLASS-FIBER FILTERS**

S.O.P. MLD 005, REVISION 5.2

November 1998

**California Air Resources Board
Monitoring and Laboratory Division**

**Engineering and Laboratory Branch
Inorganics Laboratory Section**

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1. SCOPE

This document details the acid extraction and analysis of metals from the total suspended particulates (TSP) collected on exposed, glass-microfiber filters. This revision details the method used for the analysis of arsenic (As), beryllium (Be), cadmium (Cd), and lead (Pb) by graphite furnace atomic absorption (GFAA) spectrophotometry. Also included is an overview of flame atomic absorption (Flame-AA) techniques. The same extraction solution is used for the atomic absorption analysis of As, Be, Cd, and Pb.

2. SUMMARY OF METHOD

Total Suspended Particulate (TSP) matter is collected from ambient air over a 24-hour period on a glass-microfiber filter. A 1 $\frac{3}{4}$ " by 2 $\frac{1}{4}$ " section is cut from the exposed, glass-microfiber filter. Metals from the TSP deposited on this section are extracted in dilute nitric acid by sonication with heating. The extraction solution is vacuum filtered, bottled, and stored at room temperature for later analysis by flame and graphite atomic absorption.

3. INTERFERENCES OF SAMPLE PREPARATION

- 3.1 Contamination of samples can occur from failure to clean the cutting board, scissors, and extraction vials. All cutting apparatus should be wiped thoroughly with a dry, laboratory wipe prior to each use. All sample bottles should be rinsed with a ten percent nitric acid solution prior to final rinsing with conductivity monitored DI (deionized) water.
- 3.2 Unexposed filter pieces are used as the background media for method blanks and spikes, individual, unexposed filters should be quartered, and the pieces placed together in a glassine enclosure. Careful storage of these pieces is essential for quality control. Each enclosure should be placed in a labeled, manila folder for identification purposes in the event a blank is found to be contaminated. (Label each folder with the filter's factory number, for example, 00567345.)
- 3.3 Use only DI water (for sample and standard preparation, extraction, and cleaning/rinsing of glassware) that is conductivity monitored, i.e., consistently verified to have limited contamination, such as the Nanopure Filtration System from Barnstead. Regular tap water or deionized tap water may cause contamination. Always rinse the end of the Nanopure delivery tube with clean Nanopure water prior to each use.
- 3.4 Sampling using glass-fiber filters should be limited to using only filters from manufacturer defined lots which have been determined with reasonable certainty by analysis to not interfere with the

quality of the elemental analysis of the ambient samples collected on them. If the level of contamination varies from lot to lot and/or is greater than the limit of detection, the blank value assigned each lot should be subtracted from the final result of each exposed filter for each analyte.

4. INTERFERENCES OF ANALYSIS BY INSTRUMENTATION

- 4.1 This analysis technique is susceptible to chemical, ionization, matrix, emission, and background interferences. An adequate description of the correction procedures for each is outlined in the Perkin-Elmer instrument manual, Transverse Heated Graphite Atomization (THGA): Techniques and Recommended Conditions.

5. APPARATUS AND MATERIALS

- 5.1 Atomic Absorption (AA) Spectrophotometer with a THGA graphite furnace and flame capability (Perkin-Elmer Model 5100PC); Zeeman and deuterium arc background correction; autosampler (AS-71) for furnace unit; THGA pyrolytically coated graphite tubes with integrated platforms, graphite contacts, and graphite extraction tip; furnace unit (THGA-5100ZL); cooling system; appropriate hollow cathode (HCL) or electrodeless discharge (EDL) lamps (coded or non-coded) for the desired elements; a computer (DEC-486), loaded with instrument control software (Benchtop and WINLab); and a printer (Epson LQ-570) for data handling.
- 5.2 Sonication bath with heating capability to 69°C; built-in timer.
- 5.3 Extraction vials: polypropylene, 50 milliliter (ml), equipped with snap-on polypropylene caps; glass enclosed vacuum filtration chamber; storage bottle, 4-liter, equipped with an adjustable, automatic dispensing unit with 50-ml capacity; storage bottle, 1-liter, amber glass, equipped with an adjustable, dispensing unit with 25-ml capacity.
- 5.4 Sample bottles, 60-ml, polypropylene, equipped with screw-top caps.
- 5.5 Cutting board with ruled edges; scissors, long edge.
- 5.6 Filtration membranes, 47 mm (millimeter) in diameter, 0.45 um pores, non-cellulose composition.
- 5.7 Magnetic filter funnel, polysulfone, 300-ml capacity, for use with 47 mm filtration membranes.
- 5.8 SQL Laboratory Information Management System (SQLLIMS) worklists generated via Reports Runtime program (Section 7).
- 5.9 Micropipets with polysulfone disposable tips, 10 to 2500 ul (microliter) capacity.
- 5.10 Disposable laboratory wipes (kimwipes/towels); self-adhesive labels; waterproof ink pen.

6. CHEMICALS AND REAGENTS

- 6.1 Nitric acid, HNO₃, concentrated, trace pure grade, double-distilled; diluted nitric acid solutions: 0.50 N (normal) and 0.25 N.
- 6.2 AA Grade Reference Standards, NIST traceable material, 1000 ug/ml stock, in 2% HNO₃, two separate sources (1 standard, 1 control); diluted stock solutions for calibrating standards and controls. See Section 13.
- 6.3 Matrix modifiers, atomic absorption grade: Palladium (5000 ug/ml) in nitric acid; magnesium (10,000 u/ml) in nitric acid, and phosphate (40,000 ug/ml) in nitric acid. See Section 12.4.

- 6.4 Argon gas cylinder, 99.999% purity.
- 6.5 Compressed air, with inlet particulate, oil, and water filter.
- 6.6 Acetylene gas cylinder (acetone base), Grade 5.
- 6.7 Cooling water system capable of maintaining a 2.5 L/min flow; can be either separate cooler unit or direct hookup to fresh tap water.

7. SQL LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS)

Prior to beginning sample preparation (Section 11), consult the SQLLIMS coordinator for information on the function and operating details of the computer system used to track samples and corresponding analysis results. As of this Revision, the SQLLIMS tests used for extraction and analysis, respectively, are: EXTAS and ELBAS (arsenic); EXTBE and ELBBE (beryllium); EXTCD and ELBCD (cadmium); and SACDG and SAC05 (lead).

8. GLASSWARE AND SAMPLE BOTTLE PREPARATION PROCEDURE

- 8.1 Sample bottles/caps, should be washed thoroughly with laboratory detergent, rinsed with DI water, rinsed with a ten percent nitric acid solution, and final rinsed three times with DI water. Allow the bottle to dry before recapping and storing for reuse.
- 8.2 A ten percent nitric acid solution (1:10, concentrated nitric acid: DI water) should be prepared in bulk for rinsing, and placed in a 4-liter, polyethylene bottle equipped with a dispenser.

9. REAGENT AND SPIKE SOLUTION PREPARATION

- 9.1 Prepare a 0.50 N nitric acid solution in a 1-liter volumetric flask by diluting 31.5-ml of concentrated nitric acid in DI water. In addition, prepare a 0.25 N nitric acid solution in a 1-liter volumetric flask by diluting 15.8-ml of concentrated nitric acid in DI water. Store these solutions in labeled, amber bottles.
- 9.2 Prepare a 100 ug/ml stock solution of each metal and store in acid washed, labeled, polyethylene bottles.
 - 9.2.1 For example, dilute 1000 ul of 100 ug/l arsenic to a final volume of 100 ml to yield a 1000 ng/ml solution of arsenic. Then dilute 100 ul of the 1000 ng/ml solution to a final volume of 100 ml to create a final solution of 100 ng/ml.
- 9.3 Prepare a set of standards of the above stock solutions to produce a spike solution, mix, and store in an acid washed, labeled, polyethylene bottle. The final concentration of each metal in this solution should yield a concentration at least five times the limit of detection when a 1 ml aliquot is diluted to 40 ml during extraction. A fresh spike solution should be prepared monthly.

10. EXTRACTION SPIKE AND BLANK PREPARATION

- 10.1 Extraction blanks are prepared by cutting a 1 ¾" by 2 ¼" section from an unexposed glass-microfiber filter per Section 11. (Note Interference 3.2). This section should be taken through the extraction procedures listed in Section 11. One blank should be digested along with the samples listed on the extraction worklist.
- 10.2 Extraction spikes are prepared by cutting a 1 ¾" by 2 ¼" section from an exposed or unexposed glass-microfiber filter per Section 11.6. (Note Interference 3.2). A spike should be prepared and digested with each group of samples. The sample group should include

the unspiked exposed filter sample. Exposed filter spikes are used to verify ambient filter extraction. Blank filter spikes should be used as needed to troubleshoot contamination of the system.

Pipette a 1-ml aliquot of the spike solution (Section 9.) onto the filter pieces in the test tube. Allow the filter pieces to air dry for 3 to 4 hours. Digest these with the samples as described in Sections 11.6 through 11.9.

11. SAMPLE PREPARATION PROCEDURE

- 11.1 For each sample to be extracted, use a clean extraction vial. Affix each of the previously prepared labels, including the method blanks, onto individual vials. The labels should adhere confidently, but should be removable. For best results, affix each label to the cap of the extraction vials.

- 11.2 Prepare sample barcode labels:
At the student computer, open Avery Label Pro for Win95 from the desktop. Click on the icon "open existing design." When the "open" window appears, click on the "Heavy Metals" folder and open ABCPex.lpd. A label with a barcode should appear. Click on the barcode region of the label so that it is highlighted. Right click on the mouse and scroll to Properties. In the barcode properties window, click on the data tab. Click the button labeled "serial number." Make the starting number the same as the number of the first sample on the extraction worklist (i.e. if the first sample is TP000012, the starting number should be 12). When done, exit the properties window. Print the labels by loading each sheet face up into the single feed tray and clicking the printer icon. On each label, use a waterproof pen to clearly write the extraction date and analyst's initials.

Duplicates:

To a blank label, using waterproof pen write the sample number of the duplicate. In the upper right corner label it D₂. The label on the primary sample should be labeled D₁.

Spikes:

To a blank label, using a waterproof pen write the sample number of the spiked sample, the extraction date, and in the upper right corner, label it SPK. The primary sample should be labeled S₁.

Blanks:

Using a waterproof pen, write BLANK and the extraction date on a blank label.

- 11.3 Thoroughly wash and rinse a 1-litre amber glass bottle fitted with an adjustable dispensing unit..
- 11.4 Fill this bottle with 0.50 N nitric acid. Adjust the dispenser for 20-ml aliquots; verify dispensed volume by weight. (Consider the dilute acid solution to be the same density as pure water).
- 11.5 Using a dry, disposable kintowel, thoroughly clean all cutting apparatus. Place clean, open kintowels around the immediate cutting area to prevent contamination.
- 11.6 Repeat the following steps (11.6.1 through 11.6.5) for each sample listed on the extraction worklist.
- 11.6.1 Use the cutting board to cut a 1 ¾" by 2 ¼" section of the exposed part of each filter (Figure 11.6.1, next page). Place the filter exposed-side up when cutting. Cut the filter in half, retaining the portion without the factory stamped number. Make certain that the cut halves the exposed area, and not just the entire filter. (Note: The filter may not have been exposed symmetrically, and thus cutting the filter in half may not always cut the exposed area in half.) Cut the retained half in half. Cut this portion in half and the resulting product should be a section one eighth in size of the original, exposed area of the filter and should measure 1 ¾" by 2 ¼".

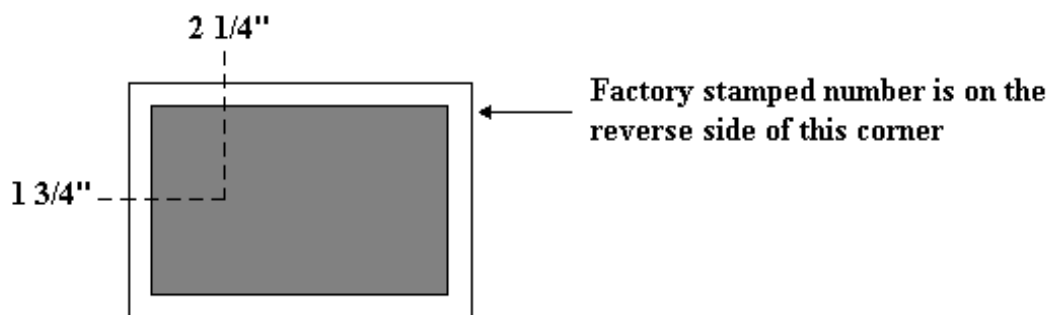


Figure 11.6.1, Exposed Filter Section.

The section removed should not be the corner with the factory-stamped number. Retain the factory-stamped corner for identification purposes. Place the remaining portions of the filter back into the glassine enclosure.

11.6.2 For duplicate samples, use the diagonal corners adjacent to the factory-stamped corner.

11.6.3 Using the long-edge scissors, cut the 1 3/4" by 2 1/4" section into half centimeter squares. This is accomplished by following the steps of cutting and folding listed below:

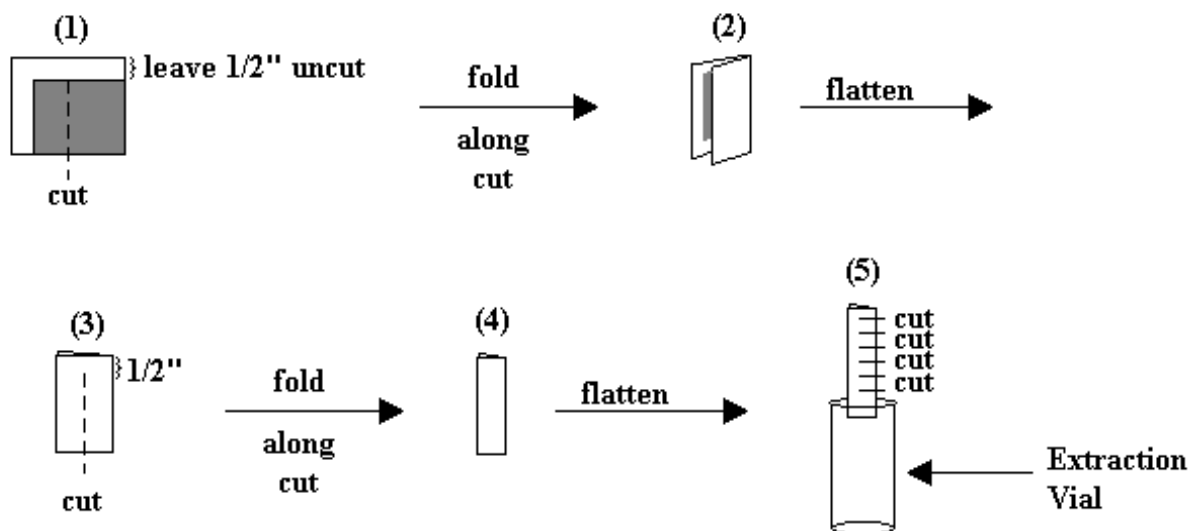


Figure 11.6.3, Cutting Filter Section.

The 1 3/4" by 2 1/4" section should be cut in half (step 1). Follow steps 2 through 5 for each half created in step 1. Cut the squares (step 5) directly into the labeled extraction vial which has the corresponding SQLLIMS number.

- 11.6.4 Next, dispense a 20 ml aliquot of 0.50 N nitric acid into the vial with the filter pieces. Be certain the acid covers all the pieces of filter. Seal the vial with a cap (note: make sure the cap "snaps" into place to assure it is on securely), place the vial in a rack, and allow to stand 12 hours at room temperature.
- 11.6.5 After twelve hours, place the filled racks 2-3 cm apart in the sonication bath.
- 11.7 Each of the samples should sonicate for one full hour at 60 ± 5 °C. Follow the manufacturer's suggestions for effective operation of the sonication bath. After the samples have sonicated with heating for one hour, dispense a 20 ml aliquot of Nanopure DI water into each vial using a 4-liter bottle equipped with a dispensing unit. Gently mix the sample solutions. Return them to the sonicating bath. Sonicate an additional hour at 60 ± 5 °C.
- 11.8 In addition to the samples on the worklist, follow steps 11.6.1 through 11.6.5 for the blanks and spikes.
- 11.9 After the samples, blanks, and spikes have finished sonicating the second time, allow the solutions to cool to room temperature. The extraction solutions should be vacuum filtered using the set-up in Figure 11.9.1.

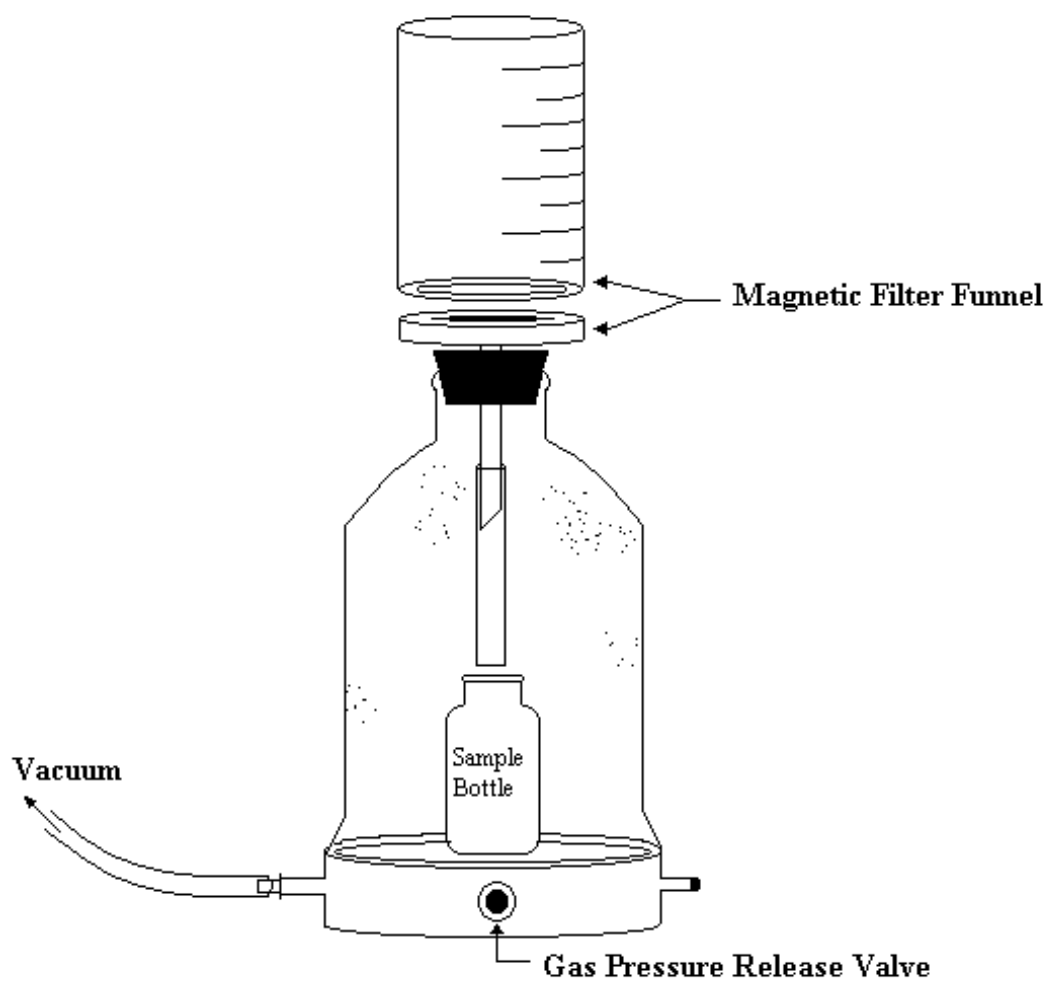


Figure 11.9.1, Vacuum Filtration Apparatus.

- 11.10 Repeat the following steps (11.10.1 through 11.10.5) for each sample listed on the extraction worklist, and the method blank and spike. Note: The magnetic filter funnel should be clean prior to use.

The spikes and blanks should be filtered after filtering all the samples listed on the extraction worklist. The filtration membrane should be rinsed with a few milliliters of DI water followed by a few milliliters of 0.25 N nitric acid prior to filtering the extraction solutions, and should be changed after every filter.

- 11.10.1 Transfer the label from the vial directly to the individual sample bottle in which the filtrate will be stored. The label should be adhered firmly and completely to the bottle, but should be easily removable.
 - 11.10.2 With the filtration membrane in place, pour the extraction solution into the magnetic filter funnel. Let the vacuum pull the liquid through. Any filter fragments or large particles should remain in the funnel.
 - 11.10.3 After almost all of the liquid has been pulled through, gently pull the gas pressure release valve several times to remove any remaining liquid, and then disconnect the apparatus carefully.
 - 11.10.4 Seal the bottle with a clean lid.
 - 11.10.5 Rinse the filtering funnel several times with Nanopure DI water to remove any particles or residue. In order to rinse the apparatus thoroughly, send a 50-ml aliquot of Nanopure DI water through the filtering apparatus with the membrane in place. Discard all rinse solutions, and reconnect the apparatus. Replace the old membrane. When replacing the old membrane, remember to discard the acid used to moisten and prepare the new membrane.
- 11.11 The extraction solution is now ready to be analyzed by atomic absorption (Section 12). Store the filled sample bottles in shallow, labeled boxes at room temperature. Samples should be organized in order by sample number.
- 11.12 Enter the extraction date for each sample on the extraction worklist (Section 7). The worklist should be filed appropriately.

12. INSTRUMENT OPERATION

- 12.1 Follow the manufacturer's operation manual for a detailed description of programming and operation of the spectrophotometer and attached peripherals. The primary 5100PC instrument control software (Perkin Elmer Benchtop and Reporter, Version 7.4) operates under Digital Equipment's GEM system; Benchtop/Reporter can be accessed from DOS prompt "C>" by typing GEM <Return>. Also available for instrument control is the Perkin Elmer WINLab, Version 2.2, software, which runs using Microsoft Windows, Versions 3.1 or higher; 'Windows '95' is preferable.
- 12.2 The following is a checklist of some items to be aware of when operating the Flame-AA. The information provided here is not intended to replace the operator's manual, but does include information not clearly or readily presented in the manual.
- 12.2.1 Lamp energies. The energy of each lamp should be recorded when used. This will highlight any lamp malfunctions or alignment problems by indicating a substantial drop in energy.

- 12.2.2 Lamp alignment. The selected line and the lamp position should be fine tuned based on the maximum energy output. Consult manual for sensitivity discussion of each line for each element. Also, note the slit width for each element.
- 12.2.3 Burner head. Positioning the burner at a 45 degree angle may be helpful for highly sensitive elements. The 10 cm head provides the best sensitivity for air-acetylene flames.
- 12.2.4 Nebulizer adjustment. Adjust/check the nebulizer whenever the aspirating chamber has been moved or whenever the characteristic concentration falls outside acceptable limits (Section 14.6). Consult operator's manual for proper adjustment of the internal spring system.
- 12.2.5 Gas flow adjustment. In addition to determining the acetylene/air ratio which gives the maximum sensitivity, be aware of analyzing elements requiring a yellow-rich flame versus a lean-blue flame. Also, be aware of the correct acetylene flow and the available tank pressure.
- 12.2.6 Impact bead and flow spoiler. The impact bead improves sensitivity for solutions considered "clean." Solutions which are high in solids or alkalines (i.e., "dirty") should be analyzed using the flow spoiler.
- 12.2.7 Deuterium lamp (continuous background correction). Fluctuation in energy (a "BOC" error) indicates possible deterioration.
- 12.3 The following is a checklist of some items to be aware of when operating the Graphite-AA. The information provided here is not intended to replace the operator's manual, but does include information not clearly or readily presented in the manual.
 - 12.3.1 Lamp energies. The energy of each lamp should be recorded when used. This will highlight any lamp malfunctions or alignment problems by indicating a substantial drop in energy.
 - 12.3.2 Lamp alignment. The selected line and the lamp position should be fine tuned based on the maximum energy output. Consult manual for sensitivity discussion of each line for each element. Also, note the slit width for each element.
 - 12.3.3 Platform and tube. The 5100PC uses a THGA graphite tube with integrated platform, which is suitable for all elements using a platformed tube, as well as those typically volatilized directly off the wall of the tube. The cooling step is not recommended when using the THGA tube. Platformed tubes (L'vov or forked) should never be used with the 5100PC. Gently wipe the cylinders with a DI water moistened cotton swab before replacing tube.
 - 12.3.4 Drying/pyrolysis/atomization setup. Consult manual for approximate temperatures and ramp times. Drying should be a smooth melt. Fine tuning of the initial pyrolysis and atomization settings can be obtained by plotting absorbance versus temperature to find the maximum absorbance.
 - 12.3.5 Quartz windows. Clean with DI water or alcohol to remove dust build-up. If windows are splattered, the drying step needs to be adjusted. Be certain windows are dry before replacing.
 - 12.3.6 Matrix modifiers. Modifiers should be used to volatilize interferences prior to atomization of the analyte, and to increase the amount of analyte atomized. Significant differences in results can be found by altering components and concentrations of the

modifiers. Plot modifier:standard ratios versus absorbance to determine maximum absorbance and minimum background.

12.3.7 Contact rings. If random peaks appear or drying times become insufficient, blow out and/or rinse with DI water the graphite cylinder to clear the inlet gas flow. If condition persists, change the contact rings.

12.3.8 Zeeman magnet. Fluctuation in energy indicates possible deterioration. Consult service technician if unable to correct by changing lamp position and/or source.

12.4 The tables below outline the setup for some specific elements.

Table 12.4.1. Outline of the Analysis of As, Be, Cd, &Pb
By Graphite Furnace Atomic Absorbtion

Analyte	Pyrolysis Temp. (°C)	Atomization Temp. (°C)
As	1300	2200
Be	1500	2300
Cd	300	1500
Pb	920	1650

Table 12.4.2. Matrix Modifiers

Analyte	Chemical Matrix Modifier
As	0.005 mg Pd + 0.003 mg Mg(NO ₃) ₂
Be	0.015 mg Mg(NO ₃) ₂
Cd	0.050 mg NH ₄ H ₂ PO + 0.003 mg Mg(NO ₃) ₂
Cd #	0.005 mg Pd + 0.003 mg Mg(NO ₃) ₂
Pb	0.050 mg NH ₄ H ₂ PO + 0.003 mg Mg(NO ₃) ₂

Yields a higher characteristic mass and a higher linear range.

Be certain to stop the flow of argon gas during the atomization step; other steps require a continuous argon flow of 250 cubic feet per minute (ft³/min). Ramp rate equals zero at this step for maximum power heating. An argon gas flow of 10 to 30 ft³/min may be required during analysis of samples with a high background interference. Generally, the background for regularly collected TSP samples is considerably low and does not require an argon purge; background correction (Zeeman or deuterium) is suggested.

13. **ANALYSIS**

13.1 Refer to Section 14 for a description of quality control measures required for this method. Historical quality control data can be found in the Inorganics Section's "Quality Control Reports."

13.1.1 Calibrate the instrument using a minimum of 3 standards; autozero using a reagent blank. These solutions must be adjusted to match the matrices of the extracted samples as close as possible, i.e., standard solutions should be adjusted to 0.25 N HNO₃ and the chemical modifier should be added similarly to both the samples and standards.

13.1.2 Verify accuracy of the calibration with a non-standard control that falls within the calibration range: the result should be within the established limits (Section 14) of the expected (target) value. If the control is out of range, the instrument may need

adjusting prior to re-calibration, or the solutions may be invalid, requiring that a new set of standards and a new control be prepared. A check of a mid-range standard should be made every ten samples. Should a standard check be greater than $\pm 10\%$ of the expected value, recalibrate and re-analyze samples back to the point where the calibration was known to be in control. The spike and blank should be treated as samples and should be analyzed along with the ambient filter samples.

14. PERFORMANCE CRITERIA

14.1 Duplicates:

In addition to the extraction blank and spike described in Section 10, every tenth sample should be extracted (and analyzed) in duplicate as a record of the method precision. The sample identification label for a duplicate should be marked with a "D₁" along with the other necessary information. The duplicates should be extracted following the steps outlined in Section 11, SAMPLE PREPARATION PROCEDURE.

If the percent difference of the duplicate results is found to be greater than twenty percent AND the mean of the two results is greater than the limit of quantitation (LOQ), then the analysis run should be evaluated. Five times the limit of detection (LOD, Section 14.4) is defined as the LOQ.

If re-analyzing the duplicate samples gives similar results, no further action is needed; if a discrepancy is found, the analysis set should be re-analyzed in total and the separate runs compared; if the runs do not compare, the entire set should be redone. The decision to re-extract all or part of the sample set should be made by case.

14.2 Blanks:

Results for blanks must be less than the analyte LOD for As, Be, and Cd, and less than two times the LOD for Pb. If greater, sample preparation and analysis procedures should be reviewed to determine extent and source of contamination, as well as validation or re-extraction and analysis requirements.

14.3 Spikes:

The spike results should be within 80-120% recovery. If exceeded, sample preparation and analysis procedures should be reviewed to determine validation, or re-extraction and analysis. Samples less than LOQ may exceed recovery limits without action.

14.4 Limit of Detection (LOD):

The limit of detection is calculated as follows:

$$\text{LOD} = |\text{X-intercept}| + (3 \text{ times the standard deviation of 7 repetitions of the lowest standard})$$

where each term is expressed in concentration units, and the |X-intercept| is the absolute value of the least squares X-axis intercept calculated from the multi-point calibration. The lowest standard must be at least one to five times the estimated LOD. This correlates with a ninety-five percentile confidence level.

Table 14.4. Limit of Detection

Analyte	Limit of Detection	
As	0.2 ng/m ³ *	2 ng/ml
Be	0.02 ng/m ³	0.2 ng/ml
Cd	0.05 ng/m ³	0.5 ng/ml
Pb	0.5 ng/m ³	5 ng/ml

* Assumes an air volume of 1600 m³.

14.5 Characteristic Mass:

The characteristic mass of each element represents the mass of analyte that yields a one percent absorbance or a 0.0044 absorbance. The characteristic mass should be determined for each new method and checked daily. The characteristic mass should be within $\pm 20\%$ of the manufacturer's expected value - the "cookbook" value. Due to the extremely low level of beryllium detected in ambient samples, the maximum allowable characteristic mass should be within the ELB's expected range. This is to allow for a possible absorbance difference found when calibrating at or very near the detection limit using the THGA. If calibrating in a higher range, the manufacturer's "cookbook" value should be adhered.

14.5.1 Equation for characteristic mass, m_o :

$$m_o = (V)(C)(0.0044) / A$$

The constant used (0.0044) is unit specific for when V is the volume of sample analyzed expressed in units of ul; C is the concentration in ug/l; and A is the determined absorbance in units of absorbance-seconds.

14.5.2 Table 4 lists the characteristic masses for some specific elements.

Table 14.5.2 Characteristic Masses for Specific Elements using THGA Tube

Char. Mass	Arsenic	Beryllium	Cadmium	Lead
Literature *	40.0	2.5	1.3	30.0
ELB **	40.0	2.4	1.3	30.0
ELB Allowable Ranges	32.0 to 48.0	2.2 to 3.6	1.1 to 1.5	24.0 to 36.0

* Literature values are from Perkin-Elmer data.

For low level Be calibrations (≤ 2 times the LOD for the lowest standard) slight absorbance variations due to normal tube and contact ring wear can greatly affect characteristic mass values. For high level calibrations ($>$ than 10 times the LOD for the lowest standard), the ELB characteristic mass values should be within $\pm 20\%$ of the literature.

** Target values can be as much as fifty percent (50%) lower when using a cap-end THGA tube.

14.6 For Flame-AA, the characteristic concentration, m_c , of the low standard should be determined for each element analyzed.

14.6.1 The characteristic concentration for Pb should be 0.45 at 283.3 nm wavelength for the ELB's Model 5100PC - Flame-AA. After cleaning the burner chamber and adjusting the nebulizer, the characteristic concentration should be within $\pm 20\%$. Since nebulizer sensitivities vary from one unit to another, sensitivities using a corrosive resistant nebulizer are lower than with the standard stainless steel nebulizer.

14.6.2 Equation for characteristic concentration, m_c :

$$m_c = (C)(0.0044) / A$$

The constant used (0.0044) is unit specific for when C is the concentration of sample analyzed expressed in units of mg/l, and A is the determined absorbance in units of absorbance.

15. TROUBLESHOOTING

15.1 Graphite-AA:

After a method has been developed and confirmed to be accurate and precise, it should not be necessary to make adjustments in the method. Changes in the drying or peak shape are indicative of problems. The items below are assuming the method has already been accurately developed.

<u>Problem</u>	<u>Possible reason</u>
High m_o	Tube or contact rings aging
Low m_o	Contaminated standards or matrix modifier
Temperature errors	Liquid low in cooling unit; inlet or outlet flow impaired
Tube error	Furnace is open; tube or contact rings damaged
Furnace error	Windows or tube missing; background correction off
Baseline dip	Dirty windows
Multiple peaks	Contact rings damaged; argon tank low
Sudden poor drying	Contact rings or tube damaged
Flattened peak	Tube aging
Peak shifted to left	Tube damaged or autosampler tip clogged
Gas pressure error	Cylinder low; pressure low
Negative results	Autozeroed incorrectly
Poor precision	Autosampler tip clogged or contaminated; standards contaminated

15.2 Flame-AA:

Problems associated with the Flame-AA are significantly less than with Graphite-AA. The items below are assuming the method and program have already been accurately developed.

<u>Problem</u>	<u>Possible reason</u>
Gas pressure error	Cylinder low; pressure low
Negative results	Autozeroed incorrectly
Poor precision	Standards contaminated
Low sensitivity	Burner head alignment or standards contaminated; lamp alignment off or lamp energy wrong
Drain error	Waste water level too high or low; drain connected improperly

16. INSTRUMENT MAINTENANCE

16.1 Routine GFAA maintenance:

- Clean quartz windows with kimwipe and alcohol.
- Condition (high temperature burn) new tubes.
- Wipe contact rings with moistened cotton swab before replacing tube.
- Check condition of contact rings.
- Check water flow inlet/outlet.
- Check argon tank pressure.
- Verify lamp energies are consistent.
- Check flushing system tubing for clogs or leaks.
- Check furnace alignment after instrument changeover.

16.2 Routine Flame-AA maintenance:

- Check condition of aspirator tubing before each use.
- Run business card in burner slot to remove lodged materials before each use. Confirm "even" flame with visual inspection.
- Verify lamp energies are consistent.
- Check drainage tubing and drain reservoir level.
- Clean burn chamber every six months. Re-adjust nebulizer per manual's instructions.
- Check burner alignment after instrument changeover.

17. INSTRUMENT OUTPUT

- 17.1 Representative peaks (analyte = solid-line; background = broken-line) for an arsenic sample using palladium/magnesium modifier (Figure 17.1.1), and a beryllium sample using magnesium modifier (Figure 17.1.2):

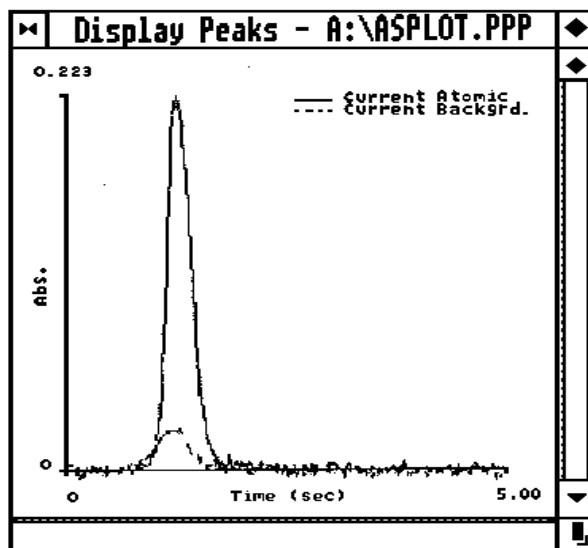


Figure 17.1.1. Arsenic Output

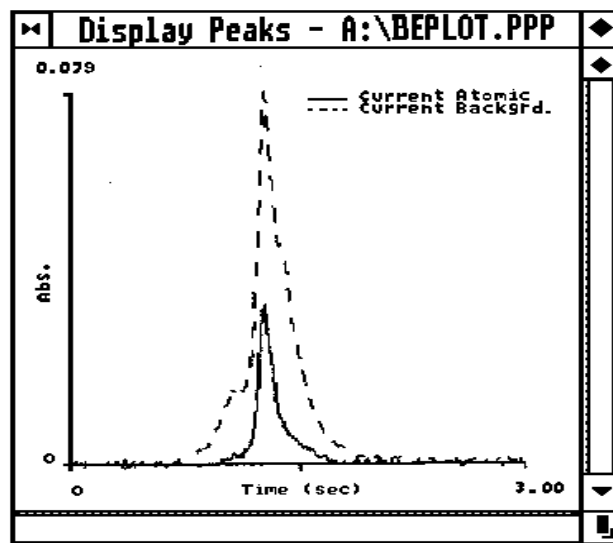


Figure 17.1.2. Beryllium Output.

18. ATOMIC ABSORPTION SCHEMATIC

- 18.1 The graphite furnace portion of the 5100PC atomic absorption spectrophotometer is represented in Figure 18.1.1 below. Light source is shown here moving through the monochromator, which isolates the wavelength of interest by dispersing the total emitted light through a series of highly polished mirrors. The detector (a photomultiplier tube) converts the intensity of light received to an electrical current that is subsequently converted to a readable output (Section 17). The Flame-AA and the Graphite-AA use the same monochromator and detector.

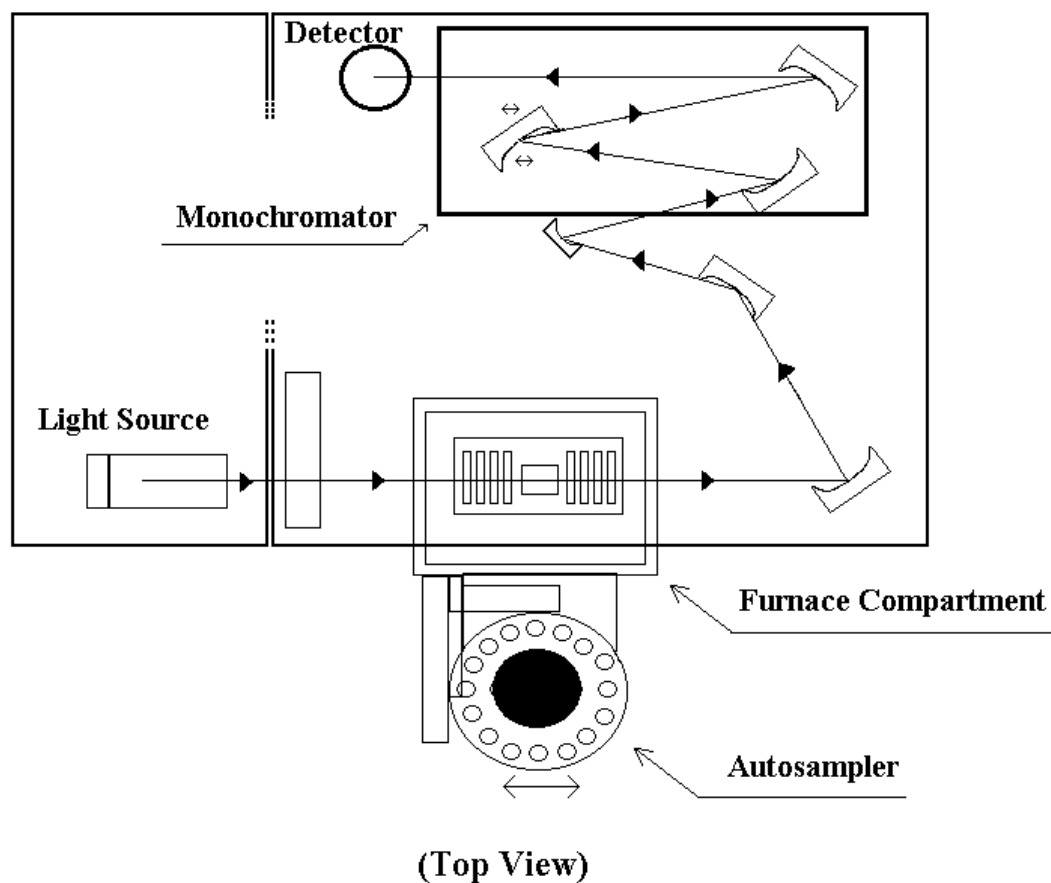


Figure 18.1.1. Atomic Absorption Schematic.

19. REVISION HISTORY

19.1 The following summarizes the history of this method:

<u>METHOD</u>	<u>EFFECTIVE DATE</u>	<u>PRIMARY CHANGE(S) FROM PREVIOUS REVISION</u>
NLB005, Preliminary Draft 2	10/28/85	Heavy metal determinations using flame; developed from EPA Method EM/SL/RTP-SOP-EMD-002 (10/83)
NLB005, Revision 3.2	09/18/88	Instrument changed from Varian 375 to Perkin Elmer (PE) 3030B; specific to lead analysis by flame
NLB005, Revision 4.0	06/01/92	Addition of arsenic, beryllium, and cadmium analyses by graphite furnace; amount of filter extracted increased by two
MLD005, Revision 5.0	04/01/93	Instrument changed from PE 3030B to PE 5100PC; analyses of lead changed from flame to graphite furnace
MLD005, Revision 5.1	01/01/97	Control software and autosampler (AS-70 to AS-71) upgrades; general fine-tuning of procedures
MLD005, Revision 5.2	07/01/98	Extraction apparatus upgrade (Section 11); general fine tuning of procedure (Section 11 and Section 14, Subsection 14.5.2); amount of filter extracted reduced by half (Sections 1 and 11)

